

PATENT COOPERATION TREATY

PCT

REC'D 24 NOV 2005

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 2003 1062	FOR FURTHER ACTION See Form PCT/IPEA/416	
International application No. PCT/FI2004/000629	International filing date (day/month/year) 2004-10-22	Priority date (day/month/year) 2003-11-07
International Patent Classification (IPC) or national classification and IPC C22B 3/42		
Applicant Outokumpu OYJ et al		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 3 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
- a. ☒ (sent to the applicant and to the International Bureau) a total of 5 sheets, as follows:
- ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
- ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
- b. ☐ (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) _____, containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

- | | | |
|-------------------------------------|--------------|---|
| <input checked="" type="checkbox"/> | Box No. I | Basis of the report |
| <input type="checkbox"/> | Box No. II | Priority |
| <input type="checkbox"/> | Box No. III | Non-establishment of opinion with regard to novelty, inventive step and industrial applicability |
| <input type="checkbox"/> | Box No. IV | Lack of unity of invention |
| <input checked="" type="checkbox"/> | Box No. V | Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement |
| <input type="checkbox"/> | Box No. VI | Certain documents cited |
| <input type="checkbox"/> | Box No. VII | Certain defects in the international application |
| <input type="checkbox"/> | Box No. VIII | Certain observations on the international application |

Date of submission of the demand 2005-08-26	Date of completion of this report 2005-11-15
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Form PCT/IPEA/409 (cover sheet) (April 2005)

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/FI2004/000629

Box No. I Basis of the report

1. With regard to the language, this report is based on:

- ☒ the international application in the language in which it was filed
☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of:
☐ international search (Rules 12.3(a) and 23.1(b))
☐ publication of the international application (Rule 12.4(a))
☐ international preliminary examination (Rules 55.2(a) and/or 55.3(a))

2. With regard to the elements of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

- ☐ the international application as originally filed/furnished
☒ the description:
pages 1 - 16 as originally filed/furnished
pages* _____ received by this Authority on _____
pages* _____ received by this Authority on _____
☒ the claims:
pages _____ as originally filed/furnished
pages* _____ as amended (together with any statement) under Article 19
pages* 18 - 22 received by this Authority on 2005-08-26
pages* _____ received by this Authority on _____
☒ the drawings:
pages 1 - 5 as originally filed/furnished
pages* _____ received by this Authority on _____
pages* _____ received by this Authority on _____

☐ a sequence listing and/or any related table(s) – see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages _____
☐ the claims, Nos. _____
☐ the drawings, sheets/figs _____
☐ the sequence listing (*specify*): _____
☐ any table(s) related to the sequence listing (*specify*): _____

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages _____
☐ the claims, Nos. _____
☐ the drawings, sheets/figs _____
☐ the sequence listing (*specify*): _____
☐ any table(s) related to the sequence listing (*specify*): _____

* If item 4 applies, some or all of those sheets may be marked "superseded."

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/FI2004/000629

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	<u>1-27</u>	YES
	Claims		NO
Inventive step (IS)	Claims	<u>1-27</u>	YES
	Claims		NO
Industrial applicability (IA)	Claims	<u>1-27</u>	YES
	Claims		NO

2. Citations and explanations (Rule 70.7)

Amended claims 1-27 were filed on 26 August 2005.

Documents cited as being of particular relevance:

D1 US 3682589

D2 WO 0134856

The invention relates to the removal of copper from a concentrated zinc sulphate solution using a silica based ion exchanger or other solid separating material of which the functional group is a polymeric amine.

D1 (abstract) discloses the removal of copper from a concentrated zinc sulphate solution using an ion exchanger. The methods of independent claims 1 and 17 differ from D1 in that the ion exchanger or other separation material is silica-based and has a polymeric amine as a functional group. The method of claim 1 also differs in that the ion exchanger is chelating alkyl-silylated. The method of claim 17 also differs in that it comprises chloride removal steps.

D2 deals with extraction of copper from solutions other than zinc sulphate solutions. D2 does not reveal an alkyl-silylated silica based ion exchanger.

D1 and D2 have been reconsidered not to be of particular relevance.

The stated differences imply improvements in reducing the use of zinc powder during solution purification of a zinc sulphate solution.

Accordingly, the invention defined in claims 1-27 is novel and is considered to involve an inventive step. The invention is industrially applicable.

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PATENT CLAIMS

1. A method for the removal of copper from a concentrated chloride-containing zinc sulphate solution known as raw solution that is going
5 to an electrolytic preparation of zinc, using an ion exchanger or other selective separation material, **characterised in that** at least some of the raw solution is routed to copper removal, which takes place using a chelating alkyl-silylated silica-based ion exchanger or other selective solid separation material, of which the functional group is a
10 polymeric amine, and that the solution from which the copper has been removed is routed to the next stage of solution purification.
2. A method according to claims 1, **characterised in that** the ion exchange stage comprises an alkaline pretreatment of the ion
15 exchanger or other selective separation material; treatment with copper-free zinc sulphate solution, the copper removal, regeneration of the ion exchanger and separation of copper from the regeneration solution.
- 20 3. A method according to claim 1, **characterised in that** the zinc content of the raw solution is in the range of 30 - 200 g/l.
4. A method according to claim 1, **characterised in that** the copper
25 content of the raw solution routed to copper removal is in the range of 100 - 2000 mg/l.
5. A method according to claim 2, **characterised in that** the treatment of the ion exchanger occurs with copper-free zinc sulphate solution, which has a pH of at least 2.
- 30 6. A method according to claim 2, **characterised in that** the copper removal with ion exchanger occurs at a pH of over 3.5.

7. A method according to claim 6, **characterised in that** the copper removal with an ion exchanger occurs at a pH of 3.7 – 4.2.
- 5 8. A method according to claim 2, **characterised in that** the copper separation from the regeneration solution is carried out as sulphide precipitation.
- 10 9. A method according to claim 1, **characterised in that** the polymeric amine acting as the functional group of the ion exchanger or selective separation material is a polyethylene imine.
- 15 10. A method according to claim 1, **characterised in that** before copper removal with an ion exchanger at least some of the raw solution is routed to a chloride removal stage.
- 20 11. A method according to claim 10, **characterised in that** before chloride removal the raw solution is cooled to a temperature of maximum 45°C.
- 25 12. A method according to claim 10, **characterised in that** before chloride removal the pH of the raw solution is adjusted to the range of 1.5 – 3.9.
- 30 13. A method according to claim 10, **characterised in that** chloride removal is performed using copper (I) oxide, cuprous oxide, so that the chloride in the solution is precipitated as copper chloride.
14. A method according to claim 13, **characterised in that** copper chloride is separated from the solution and converted with alkali back to cuprous oxide, which is at least partially routed back to chloride removal.

15. A method according to claim 10, **characterised in that** part of the raw solution is routed to cuprous oxide precipitation, where the copper in the solution is made to react with zinc powder to form cuprous oxide, and the Cu_2O generated is routed to the chloride removal stage.
16. A method according to claim 10, **characterised in that** the copper content of solution routed from the chloride removal stage to copper removal is in the range of 500 – 5000 mg/l.
17. A method for the removal of copper and chloride from a chloride-containing concentrated zinc sulphate solution, or raw solution, going to an electrolytic preparation of zinc, **characterised in that** at least some of the raw solution is routed to cooling, where the solution is cooled to a temperature of 30 – 45°C and the pH is adjusted to the range 1.5 – 3.9, after which the cooled solution is routed to chloride removal, which is performed with copper (I) oxide, Cu_2O , whereby the chloride in the solution is precipitated as copper chloride; the copper chloride is separated from the solution and the solution is routed at least partially to copper removal, which occurs using a silica-based ion exchanger or other selective solids separation material, of which a polymeric amine acts as a functional group, and where the ion exchange step comprises an alkaline pretreatment of the ion exchanger, treatment with copper-free zinc sulphate solution, copper removal, a regeneration of the ion exchanger and a separation of copper from the regeneration solution; the solution from which chloride and copper have been removed is routed to the following stage of solution purification.
18. A method according to claim 17, **characterised in that** the copper chloride is separated from the solution and converted using an alkali

back to cuprous oxide, which is at least partially routed back to chloride removal.

5 19. A method according to claim 17, **characterised in that** some of the raw solution is routed to cuprous oxide precipitation, where the copper in the solution is made to react with zinc powder to form cuprous oxide, and the Cu_2O generated is routed to the chloride removal stage.

10 20. A method according to claim 17, **characterised in that** the ion exchanger or selective separation material is chelating and has an alkyl-silylated silica base.

15 21. A method according to claim 17, **characterised in that** the zinc content of the raw solution is in the range of 30 - 200 g/l.

22. A method according to claim 17, **characterised in that** the copper content of the solution routed to copper removal is in the range of 500 – 5000 mg/l.

20 23. A method according to claim 17, **characterised in that** the treatment of the ion exchanger occurs with copper-free zinc sulphate solution, which has a pH of at least 2.

25 24. A method according to claim 17, **characterised in that** the copper removal with an ion exchanger occurs at a pH value of over 3.5.

25. A method according to claim 24, **characterised in that** the copper removal with an ion exchanger occurs at a pH value of 3.7 – 4.2.

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26. A method according to claim 17, **characterised in that** the copper separation from the regeneration solution is carried out as sulphide precipitation.
- 5 27. A method according to claim 17, **characterised in that** the polymeric amine acting as the functional group of the ion exchanger or selective separation material is a polyethylene imine.